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Inhomogeneities in Single Crystals of Cuprate Oxide Superconductors

K. Moorjani, J. Bohandy, B. F. Kim and F. J. Adrian
The Johns Hopkins University
Applied Physics Laboratory
Laurel, Maryland 20723

Abstract

The next stage in the evolution of experimental research on the high temperature superconductors will require high quality single crystals and epitaxially grown crystalline films. However, inhomogeneities and other defects are not uncommon in single crystals of cuprate oxide superconductors, so a corollary requirement will be reliable methods for judging the quality of these materials. The application of magnetically modulated resistance methods in this task will be briefly described and illustrated in this paper.

Significant and, equally important, reproducible experimental results on single crystalline samples of the cuprate oxide superconductors are now being reported. Less progress has been made on methods for assessing the quality of these samples. Ideally, such methods must be capable of probing the entire sample, a difficult requirement given that the optical opacity of these materials rules out most spectroscopic approaches. The methods that do satisfy this requirement have various drawbacks, as, for example, X-ray and neutron diffraction methods are tedious and lack the sensitivity required to detect small regions of inhomogeneity, while specific heat and other thermodynamic measurements are hard to interpret because of the limited theoretical understanding of the cuprate oxide superconductors.

Given the foregoing difficulties, the magnetically modulated resistance (MMR) methods, developed by us over the past three years and found to be ideal tools for detection of intrinsic and weak link superconductivity in both conventional and high-T_c superconductors, should play an important role in assessing the quality of crystalline superconductors. The details of the experimental implementation of the methods as well as results on powders, bulk sintered samples, thin films and single crystals have been described in detail in previous publications,[1-9] and here we will only briefly discuss the advantages of the MMR technique in revealing inhomogeneities in single crystals and thin films of high temperature superconductors. These inhomogeneities can arise from structural and chemical disorder in samples either due to inhomogeneous doping (e.g., replacement of La by Sr in La-Sr-Cu-O single crystals) or incomplete oxygenation (e.g., in Y-Ba-Cu-O single crystals) and/or the presence of defects, grain boundaries etc. (e.g., in thin film samples). The effect of these inhomogeneities is revealed in the MMR data as the presence of multiple superconducting phases and/or weak links where Josephson tunnelling, flux trapping or both can occur. As such, MMR methods are excellent tools for judging the quality of superconducting samples.

The basis of the MMR techniques lies in the magnetic field dependence of the superconducting transition as seen in the resistance measurements either at zero or any convenient frequency, ω. Consequently, with a small dc magnetic field H_o, is applied along with a modulation field, $H_m \sin \omega_m t$ ($H_m < H_o$), varying at frequency ω_m, the resistance R(T,H) can be written as,

$$R(T,H) = R(T,H_0) + \frac{\partial R}{\partial H} H_m \sin \omega_m t,$$

and a measured response is detected at the modulation frequency, ω_m, only if R is magnetic field dependent. Unlike superconducting transitions, most resistance-changing phase transitions are virtually independent of magnetic field so the former are unequivocally detected by this method. In the vicinity of the transition temperature, T_c, where the resistance drops precipitously, the response is then proportional to $(\partial R/\partial H)_{T_c} = (\partial R/\partial T)_{T_c}(\partial T_c/\partial H)$ so that for a superconducting transition ($\partial T_c/\partial H \neq 0$) one obtains a peak located at T_c and approximately proportional to $(\partial R/\partial T)$. Such a peak response has been observed in every superconducting sample of low and high T_c material examined to date[10] in the magnetically modulated electrical resistance (MAMER) configuration implemented at $\omega = 0$ and the magnetically modulated microwave absorption (MAMMA) carried out at microwave frequencies ($\omega = 9.3$ GHz). An example of MAMER in this film of the conventional superconductor niobium nitride is shown in Fig. 1.

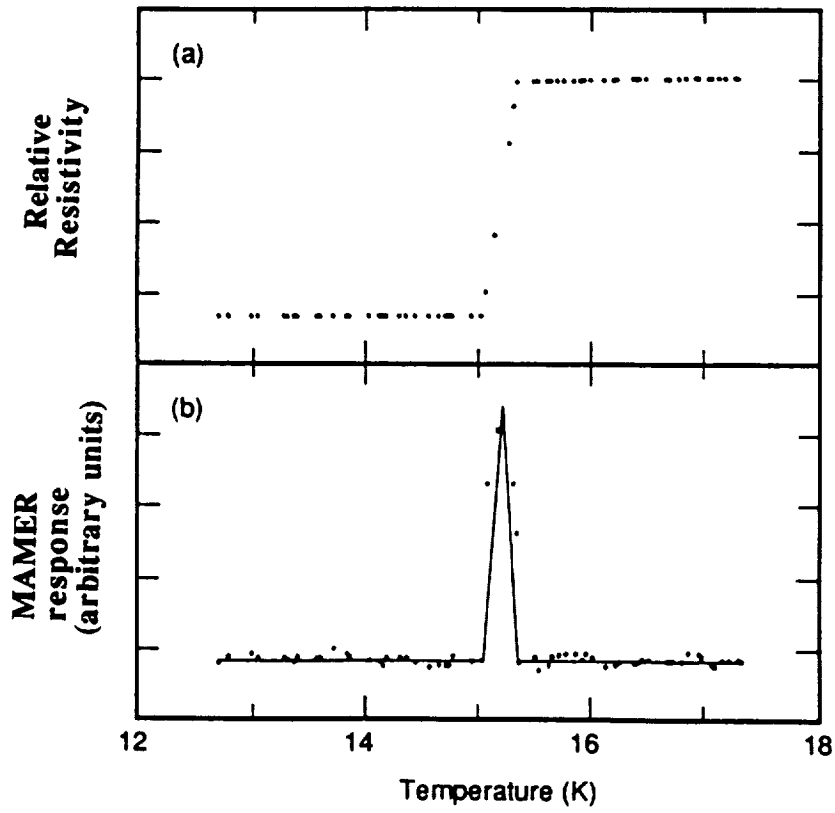

Fig. 1: The dc resistance (top) and the magnetically modulated electrical resistance (bottom) of NbN film as a function of temperature. The lines in the bottom figure are a guide to the eye.

Similarly, an example of MAMMA in a . -lt-processed, melt growth sample of $YBa_2Cu_3O_7$ is shown in Fig. 2.

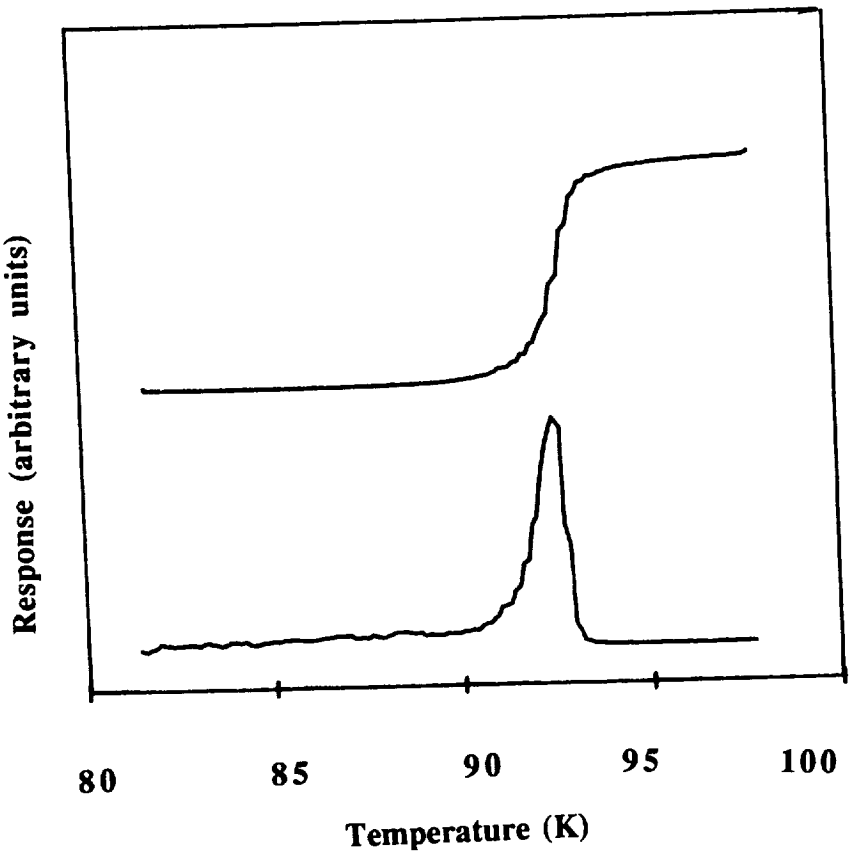

Fig. 2: Microwave absorption (top) and magnetically modulated microwave absorption (bottom) of a melt-processed, melt-growth $YBa_2Cu_3O_7$ sample.

The MMR methods become particularly useful for judging the quality of superconducting samples containing inhomogeneities in the form of multiple superconducting phases and/or weak links, that is, superconducting regions separated by non-superconducting phases. As shown elsewhere[6,11] the MAMMA and MAMER responses due to these weak links appear at temperatures below T_c and often can be distinguished from the intrinsic responses which indicate the superconducting transition itself on the basis of dependence on magnetic field, sample current, etc. In other cases the intrinsic and weak link responses can be distinguished by the aforementioned fact that only the intrinsic response is appropriately proportional to (dR/dT), which quantity can be calculated from the R vs. T curves for comparison with the MAMMA or MAMER response. Multiple superconducting phases, with T_c's less than 2 K apart, can be easily resolved as seen in Fig. 3 for a single crystal of $YBa_2Cu_3O_7$. SQUID measurements on the same sample do not resolve these two phases located at 88 K and 86.5 K but only show a diamagnetic susceptibility– that drops over a temperature spread of 3 K. As the higher T_c is only 88 K, the existence of two superconducting phases is likely to be related to incomplete oxygenation or the presence of impurities. Pure fully oxygenated samples of $YBa_2Cu_3O_7$ indeed give a single sharp peak located near 93 K as is the case for the sample shown in Fig. 2.

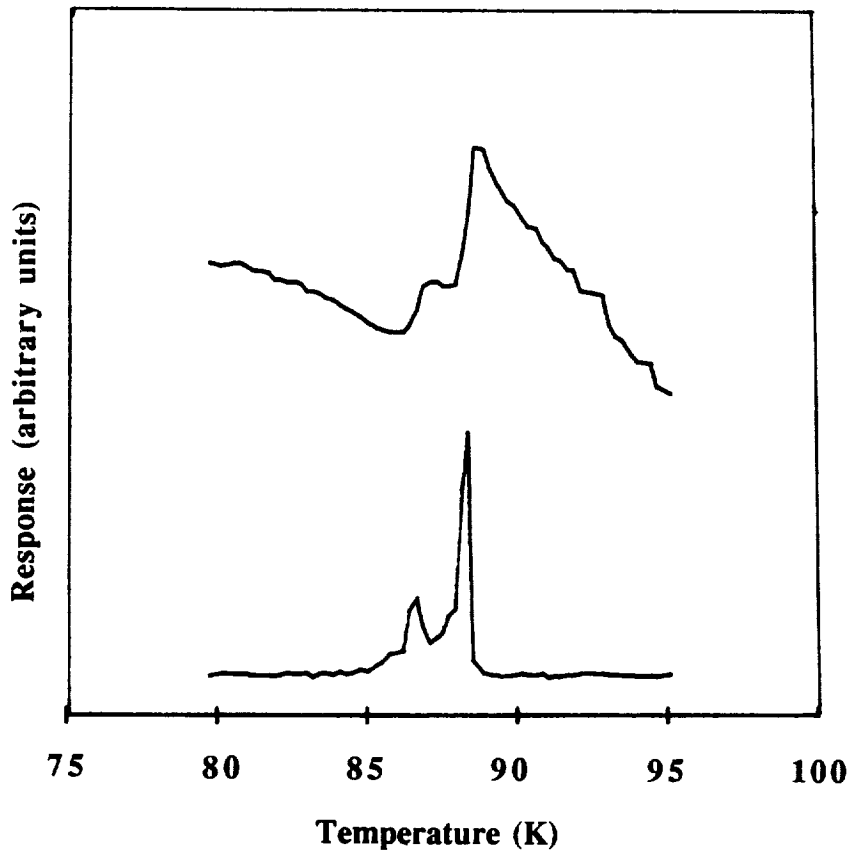

Fig. 3: Microwave absorption (top) and magnetically modulated microwave absorption (bottom) vs. temperature in a twinned single crystal of $YBa_2Cu_3O_7$.

Another example of inhomogeneity and multiple super-conducting phases is shown in Fig. 4 for a single crystal of $La_{1.88}Sr_{0.12}CuO_4$. One piece of this crystal reported on elsewhere showed a sharp drop in dc resistivity at 33 K and a broadened Meissner transition.[12] As shown in Fig. 4a, however, dc resistance measurements on the piece used here indicate a relatively sharp superconducting transition centered at a lower temperature (T_c = 29.5 K). Although there is little or no indication of multiple phases in the dc resistance measurement, the multiphasic character of the sample is clearly revealed by the presence of several closely spaced peaks in the corresponding MAMER response, also shown in Fig. 3a. The microwave resistance vs temperature, shown in Fig. 4b, shows a considerably broader superconducting transition centered at 27.9 K, while the MAMMA response shown in Fig. 4b clearly shows the presence of several different phases whose superconducting transition temperatures are spread over about 5 K.

Clearly there are significant differences between these two pieces of the same crystal of the same nominal composition. It remains to be determined whether the difference is due to inhomogeneities in Sr doping or loss of oxygen in that part of the crystal with the lower T_c. In the latter case the difference in oxygen content could have been produced during growth and/or annealing of the crystal or, alternatively, it could have taken place during the time that elapsed between the growth of the crystal and our examination of it. In any event this result highlights the need for examination of individual pieces of crystalline samples at the time they are used.

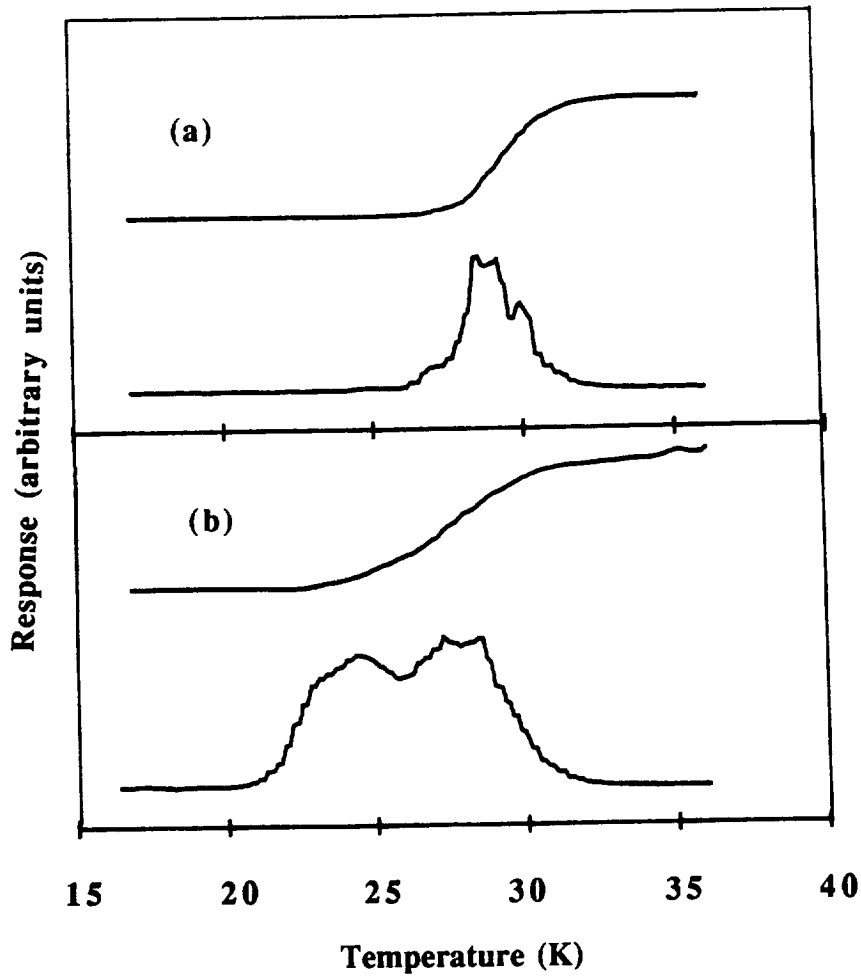

Fig. 4: (a) Electrical resistance (top) and magnetically modulated resistance (bottom) vs. temperature in a $(La_{0.94}Sr_{0.6})_2CuO_4$ single crystal.

(b) Microwave absorption (top) and magnetically modulated microwave absorption (bottom) vs. temperature in the same sample.

The difference between the dc and microwave measurements is readily understood, and shows the complementary nature of these measurements in examining all regions of the sample. The dc resistance and MAMER reflect the best superconducting path through the sample, and thus should, and does, yield the narrowest transition and highest T_c. The microwave resistance and MAMMA measurements, on the other hand, provide information about all regions of the sample penetrated by the microwaves. In the case of a single crystal sample this is primarily the surface regions as the skin depth at microwave frequencies is small compared to the crystal dimensions. In the present case the superconducting properties of these surface regions are considerably worse, particularly as regards the presence of multiple phases, than is the best superconducting path through the sample. Accordingly, microwave measurements will be especially important for examining specimens to be used in experiments involving the crystal surface.

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REFERENCES

1. K. Moorjani, B. F. Kim, J. Bohandy and F. J. Adrian, "Investigation of High Temperature Superconductivity by the Magnetically Modulated Microwave Absorption Method," Rev. Sol. State Sci. **2**, 263 (1988.)

2. J. Bohandy, T. E. Phillips, F. J. Adrian, K. Moorjani and B. F. Kim, "Detection of Superconducting Transitions by Magnetically Modulated Electrical Resistance," Mod. Phys. Lett. B, **3**, 933 (1989).

3. B. F. Kim, J. Bohandy, K. Moorjani and F. J. Adrian, "A Novel Microwave Technique for Detection of Superconductivity," J. Appl. Phys. **63**, 2029 (1988).

4. K. Moorjani, J. Bohandy, F. J. Adrian, B. F. Kim, R. D. Shull, C. K. Chiang, L. J. Swartzendruber and L. H. Bennett, "Superconductivity in Bulk and Thin Films of $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ and $Ba_2YCu_3O_{7-\delta}$," Phys. Rev. B **36**, 4036 (1987).

5. J. Bohandy, B. F. Kim, F. J. Adrian and K. Moorjani, "Particle-size and Temperature Dependence of Microwave Noise in Superconducting $YBa_2Cu_3O_{7-y}$: Evidence for Random Josephson Junctions," Phys.. Rev. B **39**, 2733 (1989).

6. B. F. Kim, J. Bohandy, T. E. Phillips, F. J. Adrian and K. Moorjani, "Detection of Weak Link Superconductivity by Magnetically Modulated Electrical Resistance," Physica C **161**, 76 (1989).

7. F. J. Adrian, J. Bohandy, B. F. Kim and K. Moorjani, J. S. Wallace, R. D. Shull, L. J. Swartzendruber and L. H. Bennett, "Magnetic Field Dependence of the Superconductivity in Bi-Sr-Ca-Cu-O Superconductors," Physica C **156**, 184 (1988).

8. B. F. Kim, J. Bohandy, T. E. Phillips, W. J. Green, E. Agostinelli, F. J. Adrian, K. Moorjani, L. J. Swartzendruber, R. D. Shull, L. H. Bennett and J. S. Wallace, "Superconducting Thin Films of Bi-Sr-Ca-Cu-O Obtained by Laser Ablation Processing," Appl. Phys. Lett. **53**, 321 (1988).

9. L. H. Bennett, D. Kaiser, L. J. Swartzendruber, J. Bohandy, B. F. Kim, F. J. Adrian and K. Moorjani, "SQUID and MAMMA Observations of the Superconducting Transition in Single Crystals of $YBa_2Cu_3O_{7-x}$,"J. Appl Phys., **67**, 5044 (1990).

10. See for example, the recent review article, "Modulation Techniques for Studying Superconductors by K. Moorjani, B. F. Kim, J. Bohandy and F. J. Adrian, to be published in the Proc. of Intl. Conf. on Superconductivity in Bangalore, India, January 10-14, 1990.

11. K. Moorjani, J. Bohandy, B. F. Kim and F. J. Adrian, "On Distinguishing Intrinsic and Weak-link Responses in Magnetically-Modulated Dissipation in High T_c Superconductors," Solid State Commun., 74, 497 (1990).

12. G. Shirane et al., "Temperature Dependence of the Magnetic Excitations in $La_{1.85}Sr_{0.15}CuO_4$ (T_c = 33 K)," Phys. Rev. Letters, 63, 330 (1989).